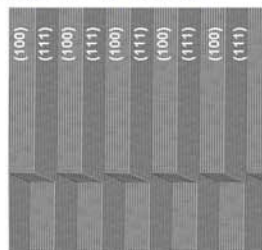


Pt(111)-(100) Nanofaceted Model Electrocatalysts

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A novel approach of preparing a one-dimensional model system for nanoparticle catalysts is presented. Unlike the stepped surfaces prepared by vicinal cuts of low-index surfaces, our preparation method provides two low-index facets, (111) and (100), connected by edges in nanoscale proximity. This (111)-(100) faceted surfaces resemble much more closely the realistic nanoparticles which have cubooctahedral shape composed of low-index (111) and (100) facets and edges.

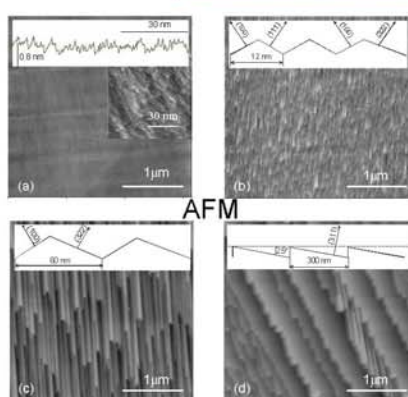
We can prepare a platinum surface consisting of (100) and (111) facets joined together by the edge



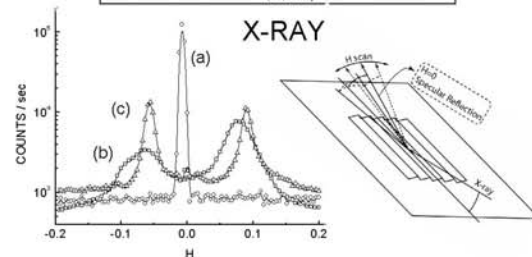
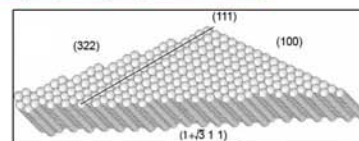
which resembles nanoparticle surfaces.



Preparation of a Platinum Surface Consisting of (111) and (100) Nano-Facets



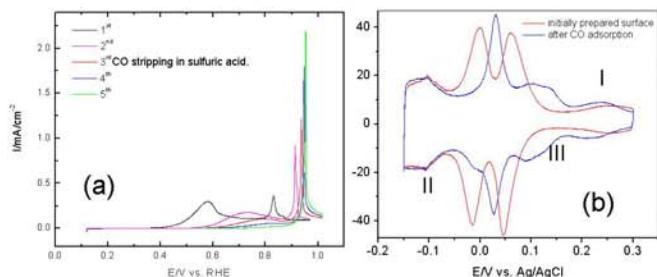
AFM



Morphologies depend on the temperature and atmosphere in which it has been annealed

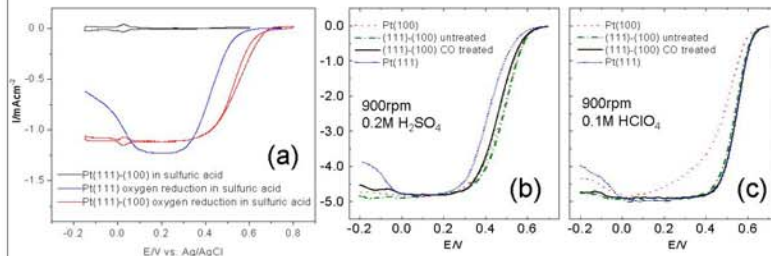
- (a) The surface, initially cut between the {111} and {100} and annealed at 1923 K in *hydrogen*, is not faceted.
- (b) The array of (111)-(100) facets formed at 1350 K in *oxygen* (facets start form at ~1000 K and their size increase as the annealing temperature increase).
- (c) Facets formed at 1450 K.
- (d) Annealing at 1923 K in presence of oxygen leads to formation of large (311) terraces. From any point in this procedure, the unfaceted surface (a) can be recovered by annealing in hydrogen atmosphere.

Electrochemical Annealing by Adsorption/Desorption of Carbon Monoxide



- (a) Dramatic disappearance of the pre-oxidation feature and the anodic shift of the oxidation peak indicate that the surface defects are electrochemically annealed by the CO adsorption/oxidation cycles.
- (b) It can also be seen in "blank" current-voltage curves; Increased sulfate peak (I), Decreased H at (110) (II), More positive onset of H at (100) (III).
- This is an example of the CO layer actively modifying the substrate. In this way, the CO layer becomes more resistant to oxidation, and binds and poisons the substrate more strongly.

Oxygen Reduction Reaction (ORR) Kinetics in Acidic Media

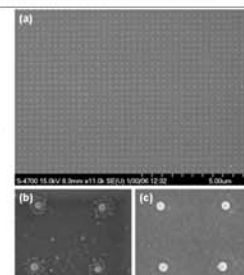


- (a) H UPD for (111)-(100) nanofaceted surface is shown with the diffusion limiting current. This indicates that UPD H does not block ORR sites.
- (b) In sulfuric acid, the ORR activity of the nanofaceted surface is the average of (100) and (111).
- (c) In perchloric acid, it is considerably better than the average indicating that the nanofaceted surface is almost twice as active as (111) which is known to be most ORR-active surface.

Future: Nano-fabricated Array Model Catalysts

Array model catalysts can be fabricated with modern lithography techniques such as focused-ion-beam or electron-beam lithography. We successfully fabricated array catalysts where millions of nanoparticles are all perfectly registered, identical in size, shape, and orientations. These array model catalysts allow molecular-level study of nanoparticles by experimental techniques developed for single-crystal surfaces or large-surface area catalysts.

- (a) Platinum nanoparticle array made by electron-beam lithography. The size of the particles can be controlled by the exposure time during lithography process. Shape of the particles can be controlled by the conditions for the initial platinum film preparation.
- (b) 30 nm hexagonal particles with (111) plane parallel with the substrate
- (c) cubooctahedral particles with (100) particles parallel with the substrate.



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